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Supported polymerisation catalysts

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### SUPPORTED POLYMERISATION CATALYSTS

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported metallocene catalysts providing advantages for operation in gas phase processes.

In recent years there have been many advances in the production of polyolefin

- 5 homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature. There have been developed several different families of metallocene complexes. In earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed,
- 10 examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

- 15 Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

- 20 The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-

borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins. in solution, slurry or gas phase. When used in the gas phase the metallocene complex 5 and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

WO 98/27119 describes supported catalyst components comprising ionic compounds comprising a cation and an anion in which the anion contains at least one substituent comprising a moiety having an active hydrogen. In this disclosure supported metallocene catalysts are exemplified in which the catalyst is prepared by treating the aforementioned ionic compound with a trialkylaluminium compound followed by 15 subsequent treatment with the support and the metallocene.

WO 98/27119 also describes a method for activating a substantially inactive catalyst precursor comprising (a) an ionic compound comprising a cation and an anion containing at least one substituent comprising a moiety having an active hydrogen, (b) a transition metal compound and optionally, (c) a support by treatment with an 20 organometallic compound thereby forming an active catalyst.

Various methods have been utilised to prepare supported catalysts of this type. For example WO 98/27119 describes several methods of preparing the supported catalysts disclosed therein in which the support is impregnated with the ionic compound. The volume of the ionic compound may correspond from 20 volume 25 percent to greater than 200 volume percent of the total pore volume of the support. In a preferred preparative route the volume of the solution of the ionic compound does not exceed substantially, and is preferably equal to, the total pore volume of the support. Such methods of preparation may be referred to as incipient precipitation or incipient wetness techniques.

More recently WO 02/06357 describes an improved incipient wetness technique 30 for the preparation of a supported metallocene catalyst system in which the support is impregnated with an ionic compound and the metallocene complex followed by

treatment with an organometallic compound.

The catalyst preparations described in the aforementioned references may typically involve a number of washing steps during both the support treatment and the impregnation of the catalyst components.

5 We have now found an improvement in the incipient wetness technique which allows for a one-pot preparation of the catalyst resulting in a more efficient procedure as well as having economic benefits.

Thus according to the present invention there is provided a one-pot method for the preparation of a supported metallocene catalyst system said method comprising the  
10 steps of:

- (i) mixing together in a suitable solvent
  - (a) an organometallic compound, and
  - (b) an ionic activator comprising a cation and an anion,
- (ii) addition of the mixture from step (i) to a support material, and
- 15 (iii) addition of a metallocene complex in a suitable solvent.

By one-pot is meant a preparation carried out without the need for washing steps and typically wherein the contact between the support material, ionic activator and metallocene is performed in a single reaction vessel.

Suitable solvents for use in the present invention include lower alkanes eg  
20 isohexane or aromatic solvents eg - toluene.

The one-pot procedure may also incorporate a final precipitation step, using for example the addition of hexane to the mixture resulting from step (iii). In this procedure a slurry or mud of the catalyst is obtained which may be used directly to inject the catalyst into the polymerisation reactor.

25 The preferred molar ratio of organometallic compound (a) to ionic activator (b) is less than 2 , preferably less than 1 and most preferably in the range 0.3 to 0.8.

The preferred metal with respect to the organometallic compound is aluminium and the preferred metal for the ionic activator is boron whereby the molar ratio of Al/B is less than 2 and is preferably less than 1 and most preferably in the range 0.3 to 0.8.

30 The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylum cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic activators are those wherein the cation of the ionic activator 5 comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate.

Typical borates suitable as ionic activators include:

- triethylammonium tetraphenylborate
- triethylammonium tetraphenylborate,
- 10 tripropylammonium tetraphenylborate,
- tri(n-butyl)ammonium tetraphenylborate,
- tri(t-butyl)ammonium tetraphenylborate,
- N,N-dimethylanilinium tetraphenylborate,
- N,N-diethylanilinium tetraphenylborate,
- 15 trimethylammonium tetrakis(pentafluorophenyl) borate,
- triethylammonium tetrakis(pentafluorophenyl) borate,
- tripropylammonium tetrakis(pentafluorophenyl) borate,
- tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
- N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
- 20 N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

A preferred type of activator suitable for use with the metallocene complexes of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

25 Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

With respect to this preferred type of ionic activator, the reaction product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an organometallic

compound, for example triethylaluminium, represents the product obtained from the aforementioned step (i).

The organometallic compound utilised in step (i) is typically chosen from those containing a metal of Groups 1- 14 of the Periodic Table but preferred organometallic compounds are those of Group 13 for example those containing aluminium.

Particularly preferred organometallic compounds are organoaluminium compounds for example trialkylaluminium compounds such as trimethylaluminium, triethylaluminium or triisobutylaluminium.

The use of triisobutylaluminium as organometallic compound has been found to lead to improved product properties in the resultant polymers, in particular improved melt strength may be achieved.

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crosfield ES70 and Davison 948 silicas.

The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

Alternative supports for the present invention are non-porous polystyrenes for example divinylbenzene crosslinked polystyrene.

The metallocene complex may comprise for example a traditional bis(cyclopentadienyl) metallocene complex or more preferably a monocyclopentadienyl complex having a 'constrained geometry' configuration.

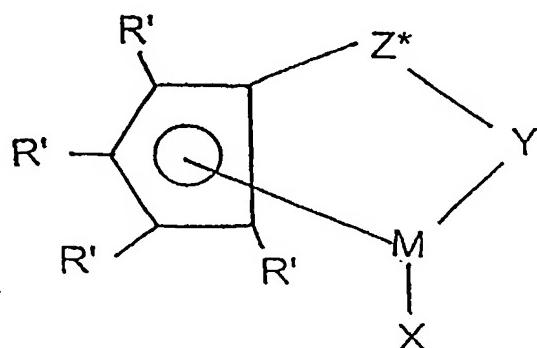
Bis(cyclopentadienyl) metallocene complexes may be represented by those disclosed in EP 129368 or EP 206794. Such complexes may be unbridged eg. bis(cyclopentadienyl) zirconium dichloride or bridged eg. ethylene bis(indenyl) zirconium dicloride. Other suitable metallocene complexes are those

5 bis(cyclopentadienyl) diene complexes described in WO 96/04290.

Examples of monocyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Particularly suitable monocyclopentadienyl complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

10 Preferred metallocene complexes for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen,  
15 hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen  
20 atoms, which forms a  $\pi$  complex with M;

Y is -O-, -S-, -NR\*-, -PR\*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>SIR\*<sub>2</sub>, CR\*<sub>2</sub>CR\*<sub>2</sub>, CR\*=CR\*, CR\*<sub>2</sub>SIR\*<sub>2</sub>, or

$\text{GeR}^*_2$ , wherein:

- R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when 5 R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system.

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-10 cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire 15 C<sub>5</sub>R'4 group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C<sub>1-10</sub> hydrocarbyl.

20 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the preparation of the supported catalysts of the present invention are those disclosed in the aforementioned WO 95/00526 and are incorporated herein by reference.

25 A particularly preferred complex for use in the preparation of the supported catalysts of the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3 -pentadiene.

The molar ratio of metallocene complex to ionic activator employed in the method of the present invention may be in the range 1:10000 to 100:1. A preferred 30 range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

The supported metallocene catalysts of the present invention are most suitable for operation in the gas phase. Gas phase processes for the polymerisation of olefins ,

especially for the homopolymerisation and the copolymerisation of ethylene and  $\alpha$ -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art. Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a 5 particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms.

10 Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms, said process performed under polymerisation conditions in the present of a supported metallocene catalyst system prepared as hereinbefore described.

15 The present invention will now be further illustrated with reference to the following examples:

Abbreviations

TEA	triethylaluminium
TiBA	triisobutylaluminium
20 Ionic Activator A	[N(H)Me(C <sub>18-22</sub> H <sub>37-45</sub> ) <sub>2</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> OH)]
Complex A	(C <sub>5</sub> Me <sub>4</sub> SiMe <sub>2</sub> N <sup>t</sup> Bu)Ti( $\eta$ <sup>4</sup> -1,3-pentadiene)

Example 1

To 3g. Ineos ES70 silica (previously calcined at 500°C for 5 hours under nitrogen, pore volume 1.55 mg/g) was added a solution made with 2.79 ml of a hexane 25 solution of triisobutylaluminium (TiBA), 1 mol/l and 1.86 ml of hexane. The mixture was allowed to react for 2.5 hours under agitation then dried under vacuum.

2 ml solution of ionic activator A (previously dried by prolonged contact with molecular sieves 4A) was reacted with 0.307 ml TiBA solution in toluene (0.265 mol/l) (molar ratio Al/B = 0.5). 1.57 ml of the resultant solution was slowly impregnated over 30 15 mins. to the above TiBA treated silica and manually agitated until no lumps were visible. The solution was left for 30 min.

0.716 ml of a solution of Complex A in heptane (9.17% wt) was then slowly

added over 15 min. and the resultant solution manually agitated until no lumps were visible. The solution was then left for 60 min followed by addition of 20 ml hexane.

The resultant suspension was agitated for 10 min. then the solid phase allowed to decant and the liquid phase removed. The catalyst was then dried under vacuum to give  
5 a loading of  $[Ti] = 40 \mu\text{mol/g}$  of catalyst and  $[Al] = 0.83 \text{ mmol/g}$  catalyst.

Polymerisation data

Run conditions

400 g of PE pellets as bed

T = 70°C

10 PC2= 6.5Bars.

C6/C2 (pressure ratio) constant at  $3510^{-4}$

SiO<sub>2</sub>/TEA impregnated used as scavenger.

H<sub>2</sub> added during the gas phase composition (50 ml).

Polymerisation time = 60min

15 Quantity of catalyst injected = 0.1 g

Activity = 74 g/ghbar

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**Claims:**

1. Thus according to the present invention there is provided a one-pot method for the preparation of a supported metallocene catalyst system said method comprising the steps of:

- (i) mixing together in a suitable solvent
  - (a) an organometallic compound, and
  - (b) an ionic activator comprising a cation and an anion,
- (ii) addition of the mixture from step (i) to a support material, and
- (iii) addition of a metallocene complex in a suitable solvent.

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**ABSTRACT**

**SUPPORTED POLYMERISATION CATALYSTS**

The present invention relates to a one-pot method for the preparation of a supported metallocene catalyst system said method comprising the steps of:

- (i) mixing together in a suitable solvent
  - (a) an organometallic compound, and
  - (b) an ionic activator comprising a cation and an anion,
- (ii) addition of the mixture from step (i) to a support material, and
- (iii) addition of a metallocene complex in a suitable solvent.

The one-pot method does not involve the previously required washing steps and allows the contact between the support material, ionic activator and metallocene to be performed in a single reaction vessel.

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